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A Superspace-Group Description of the Commensurately Modulated Structure of $TaTe_4$

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Abstract

A superspace-group description of the commensurately modulated structure of $TaTe_4$ is given on the basis of X-ray data reported by Bronsema, van Smaalen, de Boer, Wiegers, Jellinek & Mahy [*Acta Cryst.* (1987), B43, 305–313]. The structural model, given in that work, easily explains in the present approach all the observed extinction rules, including those which are not systematic limitations of space group *P*4/*ncc*. The proposed superspace group, $P^{P4/ncc}_{1\,1\,11}(00\gamma)$, with $\gamma = \frac{2}{3}$ and a $(2a \times 2a \times c)$ basic unit cell, corresponds to two possible space groups, *P*4/*ncc* and *P*4*cc*, and gives a new insight into the problem of centro- *versus* noncentrosymmetricity of the modulated structure of $TaTe_4$. It is also shown that the superspace-group description gives practically the same R factor with fewer structural parameters as compared with the space-group method. The refinements also show that the choice of space group *P*4/*ncc* (Bronsema *et al.*, 1987) is justified on the basis of the reduced number of parameters needed for the structure description. This reduction does not, at least significantly, increase the discrepancy factor R.

1. Introduction

$TaTe_4$ was first reported by Bjerkelund & Kjekshus (1964) who showed that the room-temperature basic structure* consists of interconnected infinite $TaTe_4$ antiprismatic chains. This structure is commensurately modulated and the resulting superstructure, with a $(2a \times 2a \times 3c)$ unit cell as compared with the basic one, was refined by Bronsema, van Smaalen, de Boer, Wiegers, Jellinek & Mahy (1987) within the space group (SG) *P*4/*ncc*. The same symmetry was deduced from high-resolution electron microscopy studies (Mahy, van Landyut & Amelinckx, 1987; Corbett, Hiltz, Boswell, Bennet & Prodan, 1988), and predicted by Landau theory (Walker, 1985; Sahu & Walker, 1985). However, the X-ray refinements reported by Bronsema *et al.* (1987) showed that within experimental accuracy *P*4*cc* could not be definitely excluded. Regardless of the SG, structure determination showed that the chains are modulated by forming Ta triplets, followed by Te displacements, which at the same time try to keep Te—Te distances constant. Thus, neighbouring chains are shifted in phase by approximately $2\pi/3$ with some minor deformations of the Te squares.

In the present work we show, as already suggested by Bronsema *et al.* (1987), that a superspace-group (SSG) description, originally developed for incommensurately modulated structures (de Wolff, Janssen & Janner, 1981, and references therein), is very convenient in this commensurate case as well, since it overcomes the difficulties with the SG determination. In the SSG approach the modulated structure is regarded as a cross-section (perpendicular to the internal direction $\mathbf{e}_4$) through a supercrystal, whose $(3+1)$-dimensional superspace symmetry is described by the corresponding SSG. Different cross-sections are obtained by changing the internal parameter $t = x_4 - \mathbf{qr}$, where $\mathbf{q}$ is the modulation wavevector and $\mathbf{r}$ the three-dimensional atomic position in the basic

* The basic structure is considered to be the structure without modulation (de Wolff, 1984), *i.e.* the undistorted, often hypothetical, high-temperature structure, while the average structure is obtained by averaging the modulation over the entire crystal. Both are not necessarily equivalent.

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structure. In contrast to the incommensurate cases, for commensurate modulations one supercrystal corresponds to a series of different three-dimensional structures (Fig. 1), where t becomes the phase of the modulation function $\mathbf{u}^{\mu}(x_4) = \mathbf{u}^{\mu}(\mathbf{qr} + t)$ for a given atom μ.

The analysis is based on the following data given by Bronsema *et al.* (1987):

(*a*) the basic structure (unit cell $a \times a \times c$) and the superstructure ($2a \times 2a \times 3c$) belonging to SG's *P*4/*mcc* and P4/*ncc*, respectively;

(*b*) the experimentally observed conditions limiting possible reflections:

$$\begin{cases} (HK0)\text{: } H + K = 2n \\ (0KL)\text{: } L = 2n \\ (HHL)\text{: } L = 2n \end{cases} \quad (1')$$

$$(HKL)\text{: } H = 2n \text{ and } K = 2n' \text{ for } L = 3n'' \quad (1'')$$

where indices (*HKL*) refer to the supercell ($2a \times 2a \times 3c$), but only the first group of conditions (1′) corresponds to the SG *P*4/*ncc*.

2. The basic structure

There is no (3 + 1)-dimensional SSG for tetragonal lattices possessing such internal centrings, which allow for the description of satellites ($\frac{1}{2}0\gamma$), ($\frac{11}{22}\gamma$) and their higher harmonics (de Wolff *et al.*, 1981). However, the problem can be resolved formally if the tetragonal base of the basic structure unit cell is enlarged from a into $2a$. For such a basic unit cell the modulation is described by the modulation wavevector (00γ).

In the hypothetical basic structure with unit cell ($a \times a \times c$), Ta and Te atoms are located at 2(*a*) and 8(*m*) positions of the SG *P*4/*mcc*, respectively.

To meet the formal SSG requirement, the same structure is described by a larger unit cell ($2a \times 2a \times c$) with Ta at $4 \times 2(a)$ and Te at $4 \times 8(m)$ positions, where the new x and y coordinates are related to the old x' and y' ones as $x = x'/2$ and $y = y'/2$ and where the translations (0,0,0; $\frac{1}{2},\frac{1}{2},0$; $\frac{1}{2},0,0$; $0,\frac{1}{2},0$) refer to four $TaTe_4$ square antiprismatic chains *A*, *B*, *C*, *D*, respectively.

Further, to equalize the symmetry of the basic structure with that of the complete superstructure, these positions are equivalently presented in *P*4/*ncc*. Ta atoms of columns *A* and *B*, referred to as Ta*AB* hereafter, are located at 4(*a*) and those belonging to columns *C* and *D* (Ta*CD*) at 4(*c*) positions with $z = \frac{1}{4}$. Te*AB* and Te*CD* are placed into 16(*g*) positions with $z = 0$.

For this larger unit cell the corresponding main reflections (*HKL*) are those in planes of reciprocal space with $L = 3n''$ in Bronsema's supercell ($2a \times 2a \times 3c$). From now on, they are indexed as (*hkl*), where $h = H$, $k = K$ and $l = L/3$. Further, as a result of the relationship between atomic positions of different columns in the enlarged unit cell, an additional restriction on possible reflections is obtained:

$$(hkl)\text{: } h = 2n \text{ and } k = 2n. \quad (2)$$

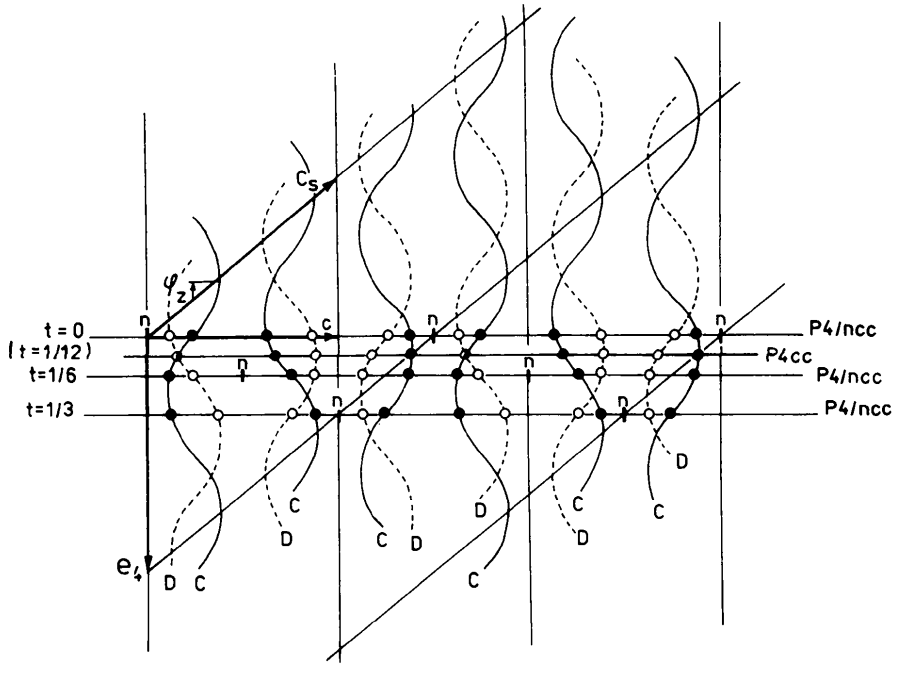

Fig. 1. The $\mathbf{c}$, $\mathbf{e}_4$ section through the supercrystal. The unit-cell base is given by $\mathbf{e}_4$ and $\mathbf{c}_s = \mathbf{c} - \frac{2}{3}\mathbf{e}_4$. Real space cross-sections, perpendicular to $\mathbf{e}_4$, shown as horizontal lines correspond to different superstructures. Wavy lines are elongated Ta atomic strings in columns *C* (continuous line) and *D* (dotted line).

3. The modulated structure

The (3 + 1)-dimensional superspace is the direct sum of two orthogonal subspaces: the three-dimensional positional (real) space and one-dimensional internal space. Hence, the (3 + 1)-dimensional operator is denoted by pairs of transformations acting in two subspaces, respectively, $\{(R|\mathbf{s}), (\varepsilon|s_4)\}$ or shorter by $(R\varepsilon|\mathbf{s},s_4)$. Any SSG operator is reduced to a single SG one if it induces three-dimensional symmetry in a given section t = constant. To find the three-dimensional operators, the SSG operators must be combined with proper translations $(E1|n_1, n_2, n_3, n_4)$ (Yamamoto & Nakazawa, 1982; Damm & Janner, 1986; van Smaalen, 1987; Janssen & Janner, 1987), where E is the identity operation. For SSG operators $(R1|\mathbf{s},s_4)$ t is invariant if $s_4 + n_4 = \mathbf{q}(n_1 + s_1, n_2 + s_2, n_3 + s_3)$ whereas for $(R\bar{1}|\mathbf{s},s_4)$ this condition changes into $s_4 + n_4 - 2t = \mathbf{q}(n_1 + s_1, n_2 + s_2, n_3 + s_3)$. Thus, depending on the value of $q_z = r/s$, SSG operators with $\varepsilon = 1$ may become SG elements, while for those with $\varepsilon = -1$ a value of t can always be chosen so that the dimensionality is reduced. Results of such analyses, performed for $P^{P4/\underline{ncc}}_{1\ 111}$ and $\mathbf{q} = (0,0,\frac{2}{3})$, are given in Table 1. The centrosymmetric SG $P4/ncc$, reported by Bronsema *et al.* (1987), is obtained for $t = n/6$ (n = integer), while for other values of t the center of symmetry is lost ($P4cc$).

To compare structural parameters obtained from the SSG with those from the three-dimensional refinement, it is necessary to determine the displacement waves as a function of atomic position $\mathbf{r}$ and modulation phase t.

The form of such a modulation function $\mathbf{u}^\mu(\mathbf{qr} + t)$ is restricted by the elements $(R\varepsilon|\mathbf{s},s_4)$ of site symmetry group K^μ (Yamamoto & Nakazawa, 1982; Yamamoto, 1982; van Smaalen, 1985):

$$\mathbf{u}^\mu(x_4) = (R\varepsilon|\mathbf{s},s_4)\mathbf{u}^\mu(x_4). \qquad (3)$$

There are no restrictions for sites 16(g) ($K^\mu = \{(E1|0000)\}$). For positions 4(c) ($K^\mu = \{(E1|0000), (C_{2z}1|0000), (C_{4z}|\frac{1}{2}\frac{1}{2}00)$ and $(C^3_{4z}|\frac{1}{2}\frac{1}{2}00)\}$) and 4($a$) ($K^\mu = \{(E1|0000), (C_{2z}1|0000), (C_{2xy}\bar{1}|00\frac{1}{2}0)$ and $(C_{2x\bar{y}}\bar{1}|00\frac{1}{2}0)\}$), where:

$$C_{2xy} = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & \bar{1} \end{pmatrix} \text{ and } C_{2x\bar{y}} = \begin{pmatrix} 0 & \bar{1} & 0 \\ \bar{1} & 0 & 0 \\ 0 & 0 & \bar{1} \end{pmatrix},$$

only z polarization is allowed. For 4(a) the modulation wave should also be an odd function.

If the superstructure primitive cell parameter along the c axis is p times that of the basic structure then the displacement field for a line of p atoms of species μ along this axis:

$$\mathbf{u}^\mu(x_4) = \mathbf{u}^\mu_0 + \sum_{n/1}^{n_{\max}} \mathbf{A}^\mu_n \cos(2\pi n x_4) + \mathbf{B}^\mu_n \sin(2\pi n x_4) \quad (4)$$

Table 1. *Three-dimensional operators and the corresponding space groups obtained from* $P^{P4/\underline{ncc}}_{1\ 111}$ *for* $\mathbf{q} = (0,0,\frac{2}{3})$ *and for some special values of the internal parameter* t

t	Three-dimensional operators*	Space group
$0, \frac{1}{2}$	$(O_1\|\mathbf{s})$ $(O_2\|s_1, s_2, 0)$ $(O_3\|s_1, s_2, \frac{1}{2})$	$P4/ncc$
$\frac{1}{6}, \frac{2}{3}$	$(O_1\|\mathbf{s})$ $(O_2\|s_1, s_2, \frac{1}{3})$ $(O_3\|s_1, s_2, \frac{5}{6})$	$P4/ncc$
$\frac{1}{3}, \frac{5}{6}$	$(O_1\|\mathbf{s})$ $(O_2\|s_1, s_2, \frac{2}{3})$ $(O_3\|s_1, s_2, \frac{1}{6})$	$P4/ncc$
Rest	$(O_1\|\mathbf{s})$ — —	$P4cc$

Notes: $(O_1|\mathbf{s})$ is $(E|000)$, $(C_{2z}|000)$, $(C_{4z}|\frac{1}{2}\frac{1}{2}0)$, $(C^3_{4z}|\frac{1}{2}\frac{1}{2}0)$, $(\sigma_x|00\frac{1}{2})$, $(\sigma_y|00\frac{1}{2})$, $(\sigma_{xy}|\frac{111}{222})$ and $(\sigma_{x\bar{y}}|\frac{111}{222})$; $(O_2|s_1, s_2, .)$ is $(I|\frac{1}{2}\frac{1}{2}.)$, $(\sigma_z|\frac{1}{2}\frac{1}{2})$, $(S_{4z}|00.)$ and $(S^3_{4z}|00.)$; $(O_3|s_1, s_2, .)$ is $(C_{2x}|\frac{1}{2}\frac{1}{2}.)$, $(C_{2y}|\frac{1}{2}\frac{1}{2}.)$, $(C_{2xy}|\frac{1}{2}\frac{1}{2}.)$ and $(C_{2x\bar{y}}|\frac{1}{2}\frac{1}{2}.)$.

* With respect to the supercell ($2a \times 2a \times 3c$).

is reduced to $n_{\max} = p/2$ and $(p-1)/2$ terms for p even and odd, respectively (Perez-Mato, Madariaga, Zuñiga & Garcia Arribas, 1987); with $q_z = \frac{2}{3}$, $p = 3$ and $n_{\max} = 1$ for $TaTe_4$. In case of equal basic and superstructure SG's ($P4/ncc$), an independent displacement function for all SSG symmetry-related positions of an atom μ describes three symmetry-independent points (see Fig. 2 for $t = 0$ and §4). Hence the displacements can be expressed with cosine-like waves:

$$u^\mu_\alpha(x_4) = u^\mu_{0\alpha} + C^\mu_\alpha \cos(2\pi x_4 + \varphi_\alpha) \qquad (5)$$

where $\alpha = x, y, z$, $C^\mu_\alpha = (B^{\mu 2}_\alpha + A^{\mu 2}_\alpha)^{1/2}$ and $\varphi_\alpha = \arctan(-B^\mu_\alpha / A^\mu_\alpha)$.

From the X-ray refinement data of Bronsema *et al.* (1987), parameters $u^\mu_{0\alpha}$, C^μ_α, φ^μ_α can be determined (Table 2). The displacements are obtained by subtraction of atomic coordinates in the superstructure and in the basic structure. Further displacements of three atoms along the axis of a column are expressed by (5). Because columns A and B, as well as C and D, are symmetry related, only parameters of one modulation function for each such pair of columns are presented in Table 2.

Two important conclusions follow from the zero-order terms of the Fourier series $u^\mu_{0\alpha}$ being very close to zero. Firstly, since the displacement wave is harmonic, the sum of three successive displacements for z, $z+1$, $z+2$ and any polarization $\alpha = x, y, z$ should be approximately equal to zero:

$$\sum_{n/0}^{2} u_\alpha[2\pi(2/3)(z+n)] \simeq C_\alpha[\cos\gamma + \cos(\gamma - 2\pi/3) + \cos(\gamma + 2\pi/3)] = 0. \quad (6)$$

This explains the relation between groups of three atoms of the same column, as noted by Bronsema *et al.* (1987), *e.g.*:

$$\Delta x[\mathrm{Te}(3)] + \Delta x[\mathrm{Te}(4)] + \Delta y[\mathrm{Te}(1)] = 0. \qquad (7)$$

Secondly, atomic positions of the average structure $\mathbf{r}^\mu_{\mathrm{av}} = \mathbf{r}^\mu_b + \mathbf{u}^\mu_0$ practically coincide with those of the basic structure $\mathbf{r}^\mu_b$ since they depend on zero-order terms of the modulation functions. These are at least two orders of magnitude smaller than the inter-

Table 2. *Modulation-function parameters obtained from the superstructure refinement by Bronsema et al. (1987)*

The modulation function parameters are given with reference to the $(2a \times 2a \times c)$ unit cell.

	Ta*AB* [4(*a*)]	Ta*CD* [4(*c*)]	Te*AB* [16(*g*)]	Te*CD* [16(*g*)]
u_{x0}	—	—	−0·00033	−0·00023
C_x	—	—	0·01074	0·00905
φ_x	—	—	166·96°	−19·38°
u_{y0}	—	—	−0·00037	−0·00027
C_y	—	—	0·00546	0·00756
φ_y	—	—	−174·54°	−74·14°
u_{z0}	0	−0·00208	0·0008	−0·0025
C_z	0·04568	0·04605	0·00877	0·00878
φ_z	−90°	33·39°	−101·18°	30·00°

atomic distances. Thus, the average and basic structures can with good approximation be taken as equivalent. As a result, the additional conditions limiting possible reflections (2) will be valid for the modulated structure as well. Rewritten into the four-index notation it becomes:

$$(hkl0)\text{: } h = 2n \text{ and } k = 2n. \qquad (8)$$

This rule follows from the expression for the modulation structure factor $F(\mathbf{H})$ (Paciorek & Łukaszewicz, 1987):

$$F(\mathbf{H}) = \sum_{\mu} \sum_{\substack{m_x, m_y, m_z \\ m_x + m_y + m_z = m}} f^{\mu} J_{m_x}(\mathbf{H}\mathbf{C}_x^{\mu}) J_{m_y}(\mathbf{H}\mathbf{C}_y^{\mu}) \times J_{m_z}(\mathbf{H}\mathbf{C}_z^{\mu}) \exp[2\pi i \mathbf{r}^{\mu}(hkl)] \exp i[m_x(\pi/2 + \varphi_x^{\mu}) + m_y(\pi/2 + \varphi_y^{\mu}) + m_z(\pi/2 + \varphi_z^{\mu})] \qquad (9)$$

where $\mathbf{H} = (hkl) - m\mathbf{q}$, $\mathbf{r}^{\mu} = \mathbf{r}_{\mathrm{av}}^{\mu} \simeq \mathbf{r}_b^{\mu}$, f^{μ} is an atomic form factor and $J_m(x)$ a Bessel function of order m. Extinction rule (8) follows from the fact that four related atoms μ of columns A, B, C, D possess approximately equal modulation amplitudes C_{α}^{μ} but different phases φ_{α}^{μ} (Table 2).

Because of the commensurability additional remarks regarding the diffraction pattern are necessary. Firstly, the structure factor $F[(hkl0)]$ includes contributions from reflection $(h,k,l,0)$, but also from satellites $(h,k,l \pm 2, \mp 3)$, $(h,k,l \pm 4, \mp 6)$, *etc.* These higher-order $(m > 2)$ satellites do not change rule (8) since they are supposed to be very weak, similar to the case of isostructural incommensurate $NbTe_4$ (van Smaalen, Bronsema & Mahy, 1986).

Secondly, the actual diffraction symmetry can be lower than that given by the SSG. From the predicted systematic conditions:

$$\begin{cases} (hk00)\text{: } h + k = 2n; & (^{n_z}_{1}) \\ (0klm)\text{: } l = 2n; & (^{c_x}_{1}) \\ (hhlm)\text{: } l = 2n; & (^{c_{xy}}_{1}) \end{cases} \qquad (10)$$

not all are realized for any given cross-section t. Conditions (10), given by $(^{c_x}_{1})$ and $(^{c_{xy}}_{1})$ are valid for any t, while that predicted by $(^{n_z}_{1})$ exists for $t = n/6$ only (Table 1), *i.e.* for the centrosymmetric superstructure SG.

These two groups of reflections (8) and (10) are consistent with all experimentally observed reflections (1). Since the first condition of (10) is a special case of the additional rule (8) it is impossible to distinguish between centrosymmetric (*P*4/*ncc*) and noncentrosymmetric (*P*4*cc*) superstructure SG's experimentally.

4. Structure refinement

The refinement was carried out using a least-squares program for commensurate structures in the framework of (3 + 1)-dimensional crystallographic symmetry. This program, written by one of the authors (IU), is a modification of the *MSRLSQ* program for incommensurate modulated structures (Paciorek & Uszyński, 1987).

Because of the memory limitation (IBM-PC) we used as input data a selected set of 3998 structure factors from the list of 6422 reflections of Bronsema *et al.* (1987).* Reflections with $|F| < 3\sigma(|F|)$ and $\theta > \theta_{\max} = 47{\cdot}7°$ were excluded. Scattering factors were taken from Cromer & Mann (1968) and an isotropic extinction correction was applied. The R values are defined as $R = \sum|(|F_o| - |F_c|)|/\sum|F_o|$.

A test refinement, using this reduced number of data converged to $R = 0{\cdot}057$ for SG *P*4/*ncc*.

Several refinements were performed for centro- and noncentrosymmetric models, since diffraction-pattern analysis (§3) allows for both possibilities. First a modulated structure refinement within SSG = $P^{P4/ncc}_{1\,111}$ and for the supercrystal cross section $t = 0$ was carried out with initial parameters transformed from those of Bronsema *et al.* (1987) (Table 2). A final R factor of 0·059 was obtained and the results are collected in Table 3.† Since no anisotropic temperature-factor modulation was taken into account the number of structural parameters as compared with the corresponding SG description was reduced by 32. In both cases the resulting R factor (Table 4) and atomic positions are practically the same (positional discrepancies were all within a standard deviation).

The number of positional parameters necessary for the complete structure description is closely connected with the problem of centro- or noncentrosymmetricity of the superstructure. The concept of

* Deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43705 (148 pp.).

† Lists of observed and calculated structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52319 (66 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Final structural parameters, obtained with superspace group* $P^{P4/ncc}_{1\,111}$, $t = 0$, *and for harmonic modulation*

Standard deviations in the last decimal places are given in parentheses. Temperature tensor components U (Å^2) are defined by $\exp(-2\pi^2\sum_i\sum_j U_{ij}h_ih_ja_i^*a_j^*)$. Isotropic extinction parameter: 1·46 (3) × 10^{-4}.

Position		Average structure	A_1	B_1
Ta*AB* 4(*a*)	z	$\frac{1}{4}$	—	0·04553 (14)
($x = \frac{3}{4}$, $y = \frac{1}{4}$)	$U_{11} = U_{22}$	0·0064 (3)	—	—
	U_{33}	0·0061 (2)	—	—
	U_{12}	−0·0004 (3)	—	—
Ta*CD* 4(*c*)	z	0·24806 (2)	0·03862 (15)	−0·02574 (16)
($x = \frac{1}{4}$, $y = \frac{1}{4}$)	$U_{11} = U_{22}$	0·0065 (3)	—	—
	U_{33}	0·0063 (2)	—	—
Te*AB* 16(*g*)	x	0·82139 (6)	−0·01054 (8)	−0·00253 (6)
	y	0·41336 (7)	−0·00544 (7)	0·00036 (6)
	z	0·00016 (3)	−0·00162 (13)	0·00860 (12)
	U_{11}	0·0091 (3)	—	—
	U_{22}	0·0079 (3)	—	—
	U_{33}	0·0092 (3)	—	—
	U_{12}	−0·0005 (2)	—	—
	U_{13}	−0·0001 (2)	—	—
	U_{23}	−0·0006 (2)	—	—
Te*CD* 16(*g*)	x	0·32182 (6)	0·00859 (7)	0·00289 (6)
	y	0·41343 (7)	0·00211 (6)	0·00748 (8)
	z	−0·00215 (2)	0·00798 (13)	−0·00462 (11)
	U_{11}	0·0090 (3)	—	—
	U_{22}	0·0086 (3)	—	—
	U_{33}	0·0090 (3)	—	—
	U_{12}	−0·0006 (2)	—	—
	U_{13}	−0·0001 (1)	—	—
	U_{23}	0·0003 (1)	—	—

Table 4. *Number of parameters and R values obtained for different superspace- and space-group descriptions*

n_{max} is the highest harmonic used during refinement.

Description	Number of parameters: Positional	Number of parameters: All	R values: $R_{m=0}$	$R_{m=\pm1}$	R_{total}
P4/ncc	22	73	0·029	0·074	0·057, 0·064*
$P^{P4/ncc}_{1\,111}$ $t = 0$ $n_{max} = 1$	22	41	0·031	0·075	0·059
P4cc	44	142			0·063*
P^{P4cc}_{111} $n_{max} = 1$	44	78	0·028	0·069	0·054
$P^{P4/ncc}_{1\,111}$ $t = 1/12$ $n_{max} = 2$	37	56	0·029	0·073	0·057

* From Bronsema *et al.* (1987) for the whole set of reflections.

atomic modulation function (AMF) (Perez-Mato *et al.*, 1987), *i.e.* a modulation function without a zero-order term in its Fourier series, is especially useful in such considerations.

In case of SSG $P^{P4/ncc}_{1\,111}$ the two AMF's describing displacements for three successive positions along z ($z \simeq z$, $z + \frac{1}{3}$ and $z + \frac{2}{3}$ with regard to the superstructure) in columns C (A) and D (B) are related by the SSG operator $(\sigma_z\bar{1}|\frac{1}{2}\frac{1}{2}00)$. They are plotted in Fig. 2 for z polarization of Te atoms in columns C and D as a function of qz. The independent AMF describes displacements of chain D for arguments $qz = \gamma + \frac{1}{3}$ and these of chain C at points $\gamma + \frac{1}{3} - 2t$.

For t equal to $n/6$ and for the centrosymmetric superstructure SG a set of three arguments for column D ($\gamma + \frac{1}{3}$) is equivalent to the set for column C ($\gamma + \frac{1}{3} - n/3$). Hence the independent AMF has to express only three displacements. In this case the same 22 positional parameters are needed in both SSG and SG approaches.

For t different from $n/6$ and for the noncentrosymmetric superstructure SG the independent AMF describes six independent displacements, thus doubling the number of modulation parameters. It can, however, happen that these six points fit a harmonic AMF well, as shown in Fig. 2. In this special case the superstructure positions, expressed by the SG method with 44 parameters, can be described in the corresponding SSG by 22 parameters only (plus one for the value of t). Other situations lead to an intermediate number of 22 to 44 modulation parameters.

In the case of a noncentrosymmetric superstructure SG the low-symmetry SSG P^{P4cc}_{111} can also be used, where AMF's for columns C and D are not related. To describe the displacement field two independent AMF's are needed, each with three modulation parameters, resulting in the same number of positional parameters as required for the SG description, *i.e.* 44.

A few refinements were performed for noncentrosymmetric models (Table 4). Firstly, a simple model with harmonic modulation of atomic coordinates and 41 free parameters only was used within the SSG $P^{P4/ncc}_{1\,111}$ for general values of t. Calculations gave three minima in R for $t = 0$, $\frac{1}{3}$ and $\frac{2}{3}$, *i.e.* for equivalent centrosymmetric solutions (see Fig. 1). This result is equivalent to the one obtained by the centrosymmetric model. Secondly, after increasing the positional parameters to 37 by taking into account second harmonics the refinement within the same SSG and for $t = 1/12$ converged to $R = 0{\cdot}057$. Finally, a

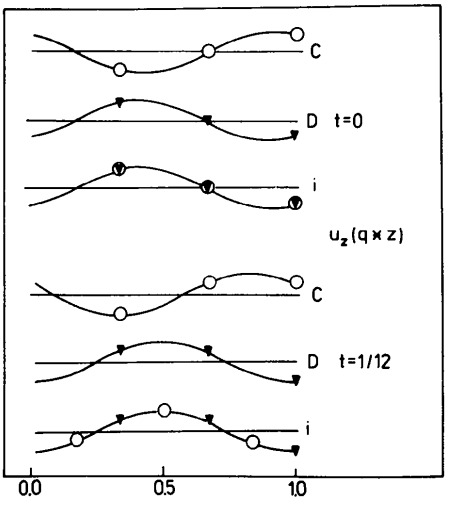

Fig. 2. Example of two AMF's for z polarization of Te atoms in columns C (○) and D (▼) related by the SSG operator $(\sigma_z\bar{1}|\frac{1}{2}\frac{1}{2}00)$. An independent AMF (denoted by 'i') should describe three independent positions for $t = n/6$ (0) and six such positions for $t \neq n/6$ (1/12).

refinement for low-symmetry SSG P^{P4cc}_{111} with harmonic displacive modulations and with 44 positional parameters was performed. It yielded an R factor of 0·054. Results of all these refinements are collected in Table 4. For the last two refinements corresponding atomic positional coordinates in the superstructure are not exactly related by the inversion centre (the discrepancy exceeds a few standard deviations). However, taking into account the number of structural parameters and the minor differences in R values obtained by different models, it can be concluded that the SSG description of the $TaTe_4$ structure at room temperature with $P^{P4/ncc}_{1\ 111}$ as well as the corresponding centrosymmetric SG $P4/ncc$, represent very good approximations.

5. Conclusions

It is shown that the room-temperature $TaTe_4$ superstructure ($2a \times 2a \times 3c$) can be described as a commensurately modulated basic structure ($2a \times 2a \times c$) with $\mathbf{q} = (00\frac{2}{3})$. The SSG $P^{P4/ncc}_{1\ 111}$ describes not only the structural symmetry and relations between coordinates of groups of atoms but also predicts extinction rules which are, together with additional conditions on reflections, in agreement with experiment. The origin of these additional limitations is also explained.

Analysis of different 'real' sections through the supercrystal gives a more general insight into the problem of centro- or noncentrosymmetricity of the room-temperature $TaTe_4$ modulated structure. The refinements show that the choice of SG $P4/ncc$ (Bronsema *et al.*, 1987) is justified on basis of a reduced number of parameters needed for the structure description. It is also shown that this reduction does not, at least significantly, increase the discrepancy factor R.

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Five-Dimensional Patterson Analysis of the Decagonal Phase of the System Al–Mn

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Abstract

A complete single-crystal X-ray data set with 1807 unique reflections has been measured for the metastable decagonal phase of the system Al–Mn with the composition $Al_{78(2)}Mn_{22(2)}$. A Patterson analysis describing the quasicrystal in five-dimensional space has been carried out in which full lattice periodicity is restored and a structure model suggested. The quasicrystal has superspace group $P10_5/mmc$ and is built up by six non-equidistant slightly puckered layers two of which are in the asymmetric unit. To a first approximation each layer can be represented by a different decorated partial Penrose pattern. With the aid of higher-dimensional Patterson analysis, the local isomorphism class was determined. Displacive

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